

FORM PTO-1390
(REV. 8-1-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

0696-0187P

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/030263

INTERNATIONAL APPLICATION NO.

PCT/FI00/00623

INTERNATIONAL FILING DATE

July 6, 2000

PRIORITY DATE CLAIMED

July 8, 1999

TITLE OF INVENTION

METHOD FOR TREATING FERTILIZER PROCESS SOLUTIONS

APPLICANT(S) FOR DO/EO/US

KARONEN, Janne and WECKMAN, Anders

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau. (WO 01/04048)
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is transmitted herewith.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 20. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO-1449(s), and International Search Report (PCT/ISA/210) with 0 cited document(s).
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
 - ✓ 1. PCT/IPEA/409
 - ✓ 2. PCT/IB/308
 - ✓ 3. PCT/IB/304
 - ✓ 4. Two (2) Sheets of Formal Drawings

U.S. APPLICATION NO (if known, see 37 CFR 1.5) <div style="font-size: 2em; font-weight: bold; margin-left: 50px;">10/030263</div>		INTERNATIONAL APPLICATION NO PCT/FI00/00623		ATTORNEY'S DOCKET NUMBER 0696-0187P	
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21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. \$1,040.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$740.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4). \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY	
				\$	1040.00
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	130.00
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	25 - 20 =	5	X \$18.00	\$	90.00
Independent Claims	2 - 3 =	0	X \$84.00	\$	0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable) Yes				\$	280.00
TOTAL OF ABOVE CALCULATIONS =				\$	1540.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	0.00
SUBTOTAL =				\$	1540.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	0.00
TOTAL NATIONAL FEE =				\$	1540.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	0.00
TOTAL FEES ENCLOSED =				\$	1540.00
				Amount to be:	\$
				refunded	\$
				charged	\$

a. ☒ A check in the amount of \$ **1540.00** to cover the above fees is enclosed.


b. ☐ Please charge my Deposit Account. No. _____ in the amount of \$ _____ to cover the above fees.
 A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-2448.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Send all correspondence to:
Birch, Stewart, Kolasch & Birch, LLP or Customer No. 2292
 P.O. Box 747
 Falls Church, VA 22040-0747
 (703) 205-8000

Date: January 8, 2002

By 
 Gerald M. Murphy, Jr., #28,977

PATENT
0696-0187P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: KARONEN, Janne et al.
Int'l. Appl. No.: PCT/FI00/00623
Appl. No.: NEW Group:
Filed: January 8, 2002 Examiner:
For: METHOD FOR TREATING FERTILIZER
PROCESS SOLUTIONS

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION

Assistant Commissioner for Patents
Washington, DC 20231

January 8, 2002

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/FI00/00623 which has an International filing date of July 6, 2000, which designated the United States of America and was published in English.--

20030103 040802

In the Claims:

Please amend the claims as follows:

4. (Amended) A method according to Claim 1, characterized in that solid matter, such as carbonate, sulphate, and oxide of alkali metals or alkaline earth metals and/or chloride, is added to the reaction mixture to partly neutralize the solution, to bind water and/or to add nutrients to the end product.

5. (Amended) A method according to Claim 1, characterized in that the solution containing urea and phosphoric acid is the scrubber solution of a urea-based NPK process, which contains or to which has been added phosphoric acid.

6. (Amended) A method according to Claim 1, characterized in that the solution containing urea and phosphoric acid is heated at 50-125 °C.

9. (Amended) A method according to Claim 6, characterized in that the solution is heated until the molar ratio of the nitrogen of the ammonia and the phosphorus of the phosphate (N/P) in the suspension is about 0.1-1.5 : 1.

10. (Amended) A method according to Claim 1, characterized in preferably being continuous and diphasic: in the first phase, water is evaporated in one or more reactors at about 100 °C,

until the moisture of the formed suspension is < 20% and the pH is 3-5 and, in a second phase, evaporation is continued in one or more reactors at about 110-115 °C, until the moisture of the suspension is < 10% and its pH is about 6-6.5.

11. (Amended) A method according to Claim 1, characterized in that the product suspension containing ammonium phosphate and/or urea ammonium phosphate is solidified in the form of a layer of 1-30 mm, preferably 10mm in thickness, spread on a sheet-iron belt conveyor, which can be heated and/or cooled, and which is heated and/or cooled for 0.01-2 hours, preferably at a retention time of 0.05-0.5 hours to a final temperature of < 50 °C.

12. (Amended) A method according to Claim 1, characterized in that the solidified end product is dried, crushed, ground and/or granulated.

13. (Amended) A solid ammonium phosphate and/or urea ammonium phosphate product, characterized in being manufactured by the method according to Claim 1.

16. (Amended) A method according to Claim 3, characterized in that the solution containing urea and phosphoric acid is heated until the moisture of the formed suspension is < 10%.

18. (Amended) A method according to Claim 3, characterized in that said solution containing urea and phosphoric acid is heated until the molar ratio of the ammonia nitrogen and the phosphate phosphor (N/P) in the suspension is about 0.85-1.5:1, preferably 1.3-1.4:1.

REMARKS

The specification has been amended to provide a cross-reference to the previously filed International Application. The claims have also been amended to delete improper multiple dependencies and to place the application into better form for examination.


Entry of the present amendment and favorable action on the above-identified application are earnestly solicited.

Attached hereto is a marked-up version of the changes made to the application by this Amendment.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By 
Gerald M. Murphy, Jr., #28,977

GMM/sll
0696-0187P

P.O. Box 747
Falls Church, VA 22040-0747
(703) 205-8000

Attachment: VERSION WITH MARKINGS TO SHOW CHANGES MADE

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE CLAIMS:

The claims have been amended as follows:

4. (Amended) A method according to [Claims 1 to 3] Claim 1, characterized in that solid matter, such as carbonate, sulphate, and oxide of alkali metals or alkaline earth metals and/or chloride, is added to the reaction mixture to partly neutralize the solution, to bind water and/or to add nutrients to the end product.

5. (Amended) A method according to Claim 1, [2 or 4,] characterized in that the solution containing urea and phosphoric acid is the scrubber solution of a urea-based NPK process, which contains or to which has been added phosphoric acid.

6. (Amended) A method according to [Claims 1 to 5] Claim 1, characterized in that the solution containing urea and phosphoric acid is heated at 50-125 °C.

9. (Amended) A method according to Claim 6, [7 or 8,] characterized in that the solution is heated until the molar ratio of the nitrogen of the ammonia and the phosphor of the phosphate (N/P) in the suspension is about 0.1-1.5 : 1.

10. (Amended) A method according to [Claims 1 to 9] Claim 1, characterized in preferably being continuous and diphasic: in the first phase, water is evaporated in one or more reactors at about 100 °C, until the moisture of the formed suspension is < 20% and the pH is 3-5 and, in a second phase, evaporation is continued in one or more reactors at about 110-115 °C, until the moisture of the suspension is < 10% and its pH is about 6-6.5.

11. (Amended) A method according to [Claims 1 to 10] Claim 1, characterized in that the product suspension containing ammonium phosphate and/or urea ammonium phosphate is solidified in the form of a layer of 1-30 mm, preferably 10mm in thickness, spread on a sheet-iron belt conveyor, which can be heated and/or cooled, and which is heated and/or cooled for 0.01-2 hours, preferably at a retention time of 0.05-0.5 hours to a final temperature of < 50 °C.

12. (Amended) A method according to [Claims 1 to 11] Claim 1, characterized in that the solidified end product is dried, crushed, ground and/or granulated.

13. (Amended) A solid ammonium phosphate and/or urea ammonium phosphate product, characterized in being manufactured by the method according to [any of the preceding Claims] Claim 1.

16. (Amended) A method according to Claim 3 [or 15], characterized in that the solution containing urea and phosphoric

acid is heated until the moisture of the formed suspension is < 10%.

17. (Amended) A method according to Claim 3, [15 or 16,] characterized in that the solution is heated until the pH of the suspension is 4-6.5.

18. (Amended) A method according to [any of Claims 3, 15-17] Claim 3, characterized in that said solution containing urea and phosphoric acid is heated until the molar ratio of the ammonia nitrogen and the phosphate phosphor (N/P) in the suspension is about 0.85-1.5:1, preferably 1.3-1.4:1.

METHOD FOR TREATING FERTILIZER PROCESS SOLUTIONS

The invention relates to a method for manufacturing a solid product that contains nitrogen and phosphor, especially a solid ammonium phosphate and/or urea ammonium phosphate product from a solution containing urea and phosphoric acid.

The invention is also directed at an ammonium phosphate and/or urea ammonium phosphate product manufactured by the method and its use as a fertilizer either alone or as part of a mixed fertilizer. The invention is also directed at a method for simultaneously manufacturing urea phosphate and a solid ammonium phosphate and/or urea ammonium phosphate containing product.

In the fertilizer process, solutions are formed and used which contain urea and phosphoric acid. As an example, the mother liquid of the urea phosphate process, which contains urea and phosphoric acid, as well as the urea containing scrubber solution of the NPK process to which phosphoric acid has been added, can be mentioned.

In the manufacture of urea phosphate, the impurities originating in the urea and the phosphoric acid used as raw material mainly remain in the mother liquid. We have to accept a low yield percentage of the end product in particular, when we want to manufacture clean, completely water-soluble urea phosphate. In that case, as much as 20 to 40% of the raw material mentioned above can remain in the mother liquid in addition to impurities. Therefore, the productivity of the urea phosphate process is to a great extent affected by how well we can utilize the raw material that remains in the mother liquid.

Various methods have been tested to utilize the mother liquid. For example, we have offered mother liquid as such to fertilizer factories that manufacture field fertilizers. However, mother liquid contains a lot of water, so that the storage and transportation costs of the solution become high, especially if the fertilizer factory is not located in the immediate vicinity of the urea phosphate factory. Furthermore, the hydrologic balance of fertilizer factories is not apt to allow additional water into the process without technical problems that mainly concern granulation, and without economic loss. During storage and transportation, salts can also precipitate from the mother liquid, causing problems in tanks when settling, and blocking tube systems.

As the viscosity of an acidic solution grows when concentrating and the solution becomes very viscous and extremely difficult to treat, concentrating the solution by evaporating water does not solve the problem.

Patent publication US 4 461 913 describes an improvement on the urea phosphate process, according to which it was possible to decrease the formation of precipitate by adding sulphuric acid, and to slightly increase the performance of the urea phosphate process; however, this improvement did not eliminate the actual problem with the mother liquid. Part of the raw material of the process still remains in the mother liquid.

Mother liquid has also been neutralized by liquefied ammonia and the formed precipitate has been filtered, resulting in a solvent fertilizer and a metalline precipitate (J. Agric. Food Chem., Vol. 29, No. 2, 1981). However, liquefied ammonia is toxic and dangerous to handle. Its safe storage, transportation, and use require special containers and treatment equipment that meet the safety criteria, making it difficult to use safely and increasing costs. The solid residual precipitate is still a disadvantage.

Urea phosphate has also been decomposed thermally to form ammonium polyphosphate (German Patent 2308408) or urea ammonium polyphosphate (US 3 713 802, Fert Res 1994, 39(1), 59-69), which can be used as fertilizers. These products are soluble but polyphosphates as such are not until they are hydrolysed to form orthophosphate, a form useful for plants. This hydrolysing is dependent on external conditions and typically slow. The original material used in these processes was pure urea phosphate and not impure mother liquid.

To avoid the problem with impurities, attempts have been made to in advance purify the phosphoric acid used as raw material (Jap. pat 49-8498). However, removing impurities from phosphoric acid is a separate, expensive process.

Furthermore, attempts have been made to render mother liquid a suspension that could be used as such (CA 112:20428, PL 146113B2, Fert Res 1994, 39 (1), 59-69) by adding clay mineral and other nutrients. However, the suspension thus obtained still continues a lot of water, limiting its use to the immediate vicinity. Moreover, special equipment is required to spread it in the fields.

The present invention is directed at a method for manufacturing a solid product containing nitrogen and phosphor, especially an ammonium phosphate and/or urea ammonium phosphate product from process solutions containing urea and

phosphoric acid; for example, from the mother liquid of a urea phosphate process or from the scrubber solution of the NPK process to which phosphoric acid has been added, by heating the said solution in a reactor, so that the urea contained by the mother liquid is decomposed into ammonia and carbon dioxide. The carbon dioxide and the forming water vapour are evenly removed from the reactor by suitable agitation and, at the same time, effervescence/foaming is prevented.

The ammonia generated by the decomposition neutralizes the phosphoric acid in the mother liquid, so that a suspension containing ammonium phosphate and/or urea ammonium phosphate is generated, possibly also containing other salts, phosphates or sulphates, for example, depending on the origin of the initial material used.

The suspension thus obtained is solidified by cooling, dried, crushed, ground, and/or granulated to form a product that contains nitrogen and phosphor, an ammonium phosphate and/or urea ammonium phosphate product in particular.

The invention is also directed at a solid product containing nitrogen and phosphor, manufactured by the method, an ammonium phosphate and/or urea ammonium phosphate product in particular, and its use as a fertilizer either alone or as part of a mixed fertilizer.

We observed that the urea and the phosphoric acid of various process solutions containing urea and/or impure phosphoric acid, as well as the other salts possibly contained by them as impurities, such as sodium salt, potassium salt, calcium salt, magnesium salt, iron salt, manganese salt, could be utilized by the method according to the invention by manufacturing from them a solid product that dissolved well in water and almost completely in an ammonium citrate solution and contained nitrogen and phosphor, an ammonium phosphate and/or urea ammonium phosphate product in particular. The product as such can be used as a fertilizer or it can be used as raw material in manufacturing mixed fertilizers.

In addition to the mother liquid of the urea phosphate process and the phosphoric acid treated scrubber solution of the NPK process, for example, agricultural residual solutions containing urea, phosphoric acid solutions generated by the surface finish of metal, the solids-bearing phosphoric acid suspensions in the sedimentation of phosphoric acid, or their mixtures are suitable to be used as initial solutions in the method according to the invention. Phosphates precipitated by water purification can also be utilized as part of the feed material.

When e.g. the mother liquid of the urea phosphate process is heated, the following actions can be effected at the same time: 1) evaporation of water, 2) decomposition of urea into ammonia and carbon dioxide, and 3) a neutralizing reaction of the generated ammonia with phosphoric acid. Adjusting the temperature and the reaction time can control these three phases of reaction.

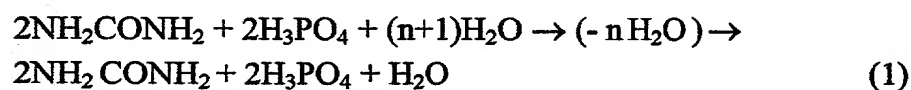
The rate of decomposition of urea mainly depends on the temperature and the pH of the solution. Although urea is decomposed at relatively low temperatures, beginning from about 50 °C, the reaction time becomes fairly long, when considering practical applications; especially, if the initial solution has high water content. Raising the temperature to about 80 °C guarantees a sufficient reaction rate and evaporation speed of water.

On the other hand, when the temperature increases to more than 125 °C, this causes the formation of unwanted polyphosphates, which as such are not usable as plant nutrients but require a hydrolysis before use. The formation of polyphosphates can be avoided by adjusting the temperature of the reaction solution to about 110-115 °C maximum, for example, by adjusting the pressure used for heating and the heating time. Using over-pressure or vacuum can enhance the adjustment of the reaction temperature and, at the same time, that of the reaction time, when needed. By means of conventional means, the process can use vacuum to evaporate water, so that we can operate at a lower temperature than in normal pressure. Correspondingly, urea can be decomposed in over-pressure with lesser evaporation of water.

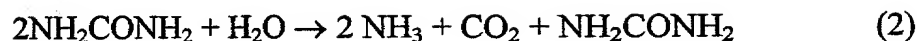
In order to manufacture a solid end product containing ammonium phosphate and/or urea ammonium phosphate by using the method according to the invention, the molar ratio (N/P) of the nitrogen of the urea and the phosphorus of the phosphoric acid in the initial solution must be 0.85 at the minimum. If the molar ratio is lower, solidification becomes considerably more difficult or it does not occur at all.

In the following, the various stages of the method according to the invention are presented by simplified reaction formulas (1) – (3), and the formation of polyphosphate by formula (4).

Evaporation of water:



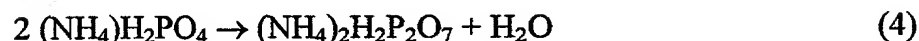
Decomposition of urea:



Formation of ammonium phosphate:



5 Formation of polyphosphate:



10 The method according to the invention can be applied both in batches and as a continuous process either in single or multiple stages. When the method is applied in batches, the molar ratio of the ammonia and the phosphoric acid ($\text{NH}_3:\text{H}_3\text{PO}_4$) at the end of the neutralizing reaction is about 1, increasing, together with the fine-grained compounds, such as iron phosphates that are generated at the beginning of the neutralizing phase, the viscosity of the formed suspension into the range ($>1000\text{cP}$), in which the suspension is at its toughest and fairly difficult to treat. The removal of water vapour and carbon dioxide from the suspension also becomes
15 more difficult, the risk of effervescence and foaming grows and the water content of the suspension remains fairly high.

These problems are avoided in the continuous process. The neutralizing reaction in particular can be continued past the molar ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1$, and in this way we can decrease the viscosity of the suspension.

20 It is most preferable to apply the method according to the invention as a continuous, two-phase process, whereby the two-phase aspect may also refer to the use of several successive reactors placed in series. The advantage is mainly achieved because of an easier gas treatment and a superior control of viscosity.

25 In that case, an initial solution, such as the mother liquid of the urea phosphate process, is heated in a first overflow reactor at $80-125^\circ\text{C}$, preferably at about $90-100^\circ\text{C}$, until the majority of the water contained by the initial solution has evaporated and the urea has decomposed, forming about $2/3$ of the ammonia required for neutralizing the free phosphoric acid in the solution.

30 As a consequence of the neutralizing reaction, a suspension containing ammonium phosphate and/or urea ammonium phosphate is generated, the water content of which is $15-20\%$ and which is still so acidic ($\text{pH} < 4$) that the ammonia remains in

the form of a dissolved ammonium ion. The viscosity of the suspension is typically less than 1000 cP.

At this stage, only water vapour and carbon dioxide in the form of gases exit the reactor. To prevent foaming/effervescence and to ensure a controlled removal of gases, the reaction mixture is constantly agitated and, when needed, a small amount of a conventional anti-foaming agent can be added. By adding water, an increase in viscosity to a harmful range can be prevented, as well as an excessive increase in the temperature.

The suspension is conveyed from the first reactor to a second reactor where heating is continued at about 110-115 °C, until the water content of the suspension is low (<10% H₂O), pH about 6-6.5, which corresponds to a molar ratio of about 1.3-1.4 of ammonia and phosphoric acid (NH₃:H₃PO₄). In that case, the viscosity of the suspension is as low as possible. In addition to water vapour and carbon dioxide, some ammonia gas is released from the reactor, which can be recovered by a scrubber by washing it with mother liquid and returning it to the first reactor.

As evaporating water binds the excess heat, the reaction is safe. However, both reactors must have sufficient mixing in order for the generated gas to easily exit the reaction mixture. The boiling point of the mixture determines the temperature of the reactor, being about 100 °C in the first reactor and about 110-115 °C in the second reactor.

By suitably selecting the retention time, the vapour temperature, and the heating surface area, the three reactions mentioned above can be adjusted to take place as desired. In the first phase, the solution is concentrated to a concentration in which its water content is about 20-40%, and the molar ratio NH₃:H₃PO₄ is about 0.7-0.8, and in the second phase to a concentration in which its water content is about 5-10% and the molar ratio NH₃:H₃PO₄ about 1.3-1.4.

Finally, the generated, strong solution is solidified by any conventional method used for the manufacture of fertilizers. A sheet-iron belt that can be cooled or heated is very well adapted to solidification. If we want to continue the reaction on the belt, the forward end of the belt can be heated at the same time as its tail is cooled.

The product is preferably and quickly solidified, when the suspension has been spread on the sheet-iron belt or plate as a thin layer and it is cooled to below 60 °C. Solidification takes place already in 1-5 minutes, if the thickness of the suspension layer is 2 mm, and in about 20-30 minutes, when it is 10-20 mm.

The solid, plate-like product can be dried, crushed, ground and/or granulated and, when needed, classified by screening; the too rough and fine-grained parts are returned to the second reactor. In addition to the end product, or instead of it, other nutrients or, for example, salts that bind water can be fed into the second reactor.

- 5 The end product as such can be used as NP fertilizer, or it can be used for the manufacture of NPK fertilizer, for example, preferably by feeding into the second reactor a suitable source of potassium, such as KCl, K_2SO_4 or K_2CO_3 . Potassium carbonate also has an advantageous effect that enhances neutralization.

- 10 $CaCO_3$ or CaO are also effective both as nutrients and additive neutralizers. Furthermore, they advance the drying of the product by binding water. Correspondingly, hemi hydrate $CaSO_4 \cdot 0.5 H_2O$ or kieserite (kiseriitti) $MgSO_4 \cdot H_2O$ both bind water and give nutrients.

- 15 The mother liquid contains most of the other nutrients (Ca, Mg, S) and micro-nutrients (B, Cu, Zn, Mn, Fe, Mo, Cl) required, to a sufficient extent, but even if the content of some nutrient were too low, they are easy to add to the second reactor.

If there is a need to bind part of the metals of the mother liquid, for example the iron, to a soluble form, the reaction temperature can be increased to 125 °C so that the desired part of the phosphor is in the form of pyrophosphate, which makes these metals complex.

- 20 The physical and chemical properties of the solid end products according to the invention meet the quality requirements made of typical field fertilizers.

- 25 Table 1 shows the chemical analysis of the mother liquid of two different urea phosphate processes. Raw material of different origins was used in the processes. The results give a picture of typical amounts of impurities contained by the mother liquid.

Table 1 The chemical analyses of the mother liquid

Compound	Mother liquid 1	Mother liquid 2
Urea-N (w-%)	10.8	11.1
NH ₄ -N (w-%)	0.48	1.5
P ₂ O ₅ -tot (w-%)	27.8	27.8
Cl (w-%)	<0.02	0.02
F (w-%)	0.87	0.81
Al (w-%)	0.22	0.35
Cr (ppm)	8.8	160
Fe (w-%)	0.88	0.66
Mg (w-%)	1.8	1.1
S (w-%)	1.2	1.3
H ₂ O-KF (w-%)	26.7	28.2

Drawings

Flow chart 1 describes the simultaneous manufacture of urea phosphate and an ammonium phosphate and/or urea ammonium phosphate product.

Flow chart 2 describes in detail the manufacture of the ammonium phosphate and/or urea ammonium phosphate product.

The following examples describe in detail the various alternative implementations of the invention without limiting it.

Example 1a

The initial material was urea phosphate mother liquid 2, the chemical analysis of which is presented in Table 1.

The test used a 5-litre overflow reactor that was provided with agitation and jacketing. 5.1kg of mother liquid with a pH of 2.1 as a 10% solution and a water content of 27.4%, and anti-foaming agent Fennodefo 380 were added to the reactor. First, the temperature of the mother liquid was raised to 100 °C. During the first hour, the temperature was further raised to 111 °C. Along with the decomposition of the urea, the pH increased from 2.1 to 2.7. During the second hour, the temperature was kept stable and the pH increased to 5.4. A little water (0.35kg) was added because of excessive evaporation.

The test was continued on a continuous-action basis by feeding mother liquid from the urea phosphate process into the reactor at a rate of about 2kg/hour. At first, a small amount of water was added (0.2kg). After a three-hour run, the conditions were stabilized (111 °C, pH 5.9, 1500cP, 9.9% H₂O). After a one-hour smooth running, the feeding was stopped and the formed suspension was allowed to continue mixing at the same temperature. After twenty minutes, the suspension was clearly thinner (111 °C, pH 6.2, 400cP, 7.8% moisture). When the evaporation time was extended, the viscosity began to increase again and after 40 minutes we started to cool the suspension (111 °C, pH 6.4, 1000cP, 7.6% moisture). When the agitation was stopped, the gas formation was so minor that the swelling of the suspension was no longer a problem.

The suspension was poured on two plates, one of which was cooled (23 °C) with water from below and the other one was at room temperature without cooling. The suspension on the cooled pan started hardening after 11 minutes (47 °C) and had hardened after 27 minutes (35 °C). The other plate was slower to cool and hardened after 64 minutes (46 °C). The solid plates were kept overnight (23 °C), crushed three times by a jaw crusher and analysed (Table 2).

Example 1b

This test was conducted in the same way as Test 1a but at a higher temperature. Adding 5kg of mother liquid to the reactor started the test. During the batch reaction (2h 40min), the temperature was raised from 100 °C to 124 °C and the pH increased from 2.1 to 5.8. The steam exiting the reactor was still neutral at the final stage.

The test was continued on a continuous-action basis by feeding about 2.8 kg of mother liquid per hour. After half an hour, 1 kg of water was added, which decreased the temperature for a while. After two hours, the conditions were stable (121 °C, pH 6, 800cP, 12.5% moisture). The reaction was continued for another 3 hours at the same temperature (120-122 °C), during which time the viscosity remained the same (800cP), the pH increased (pH 6.4), and the moisture decreased (9.7%). The measurements of the final suspension slightly changed (121 °C, pH 6.4, 1400cP, 8.1% moisture), when feeding was stopped.

The suspension was poured on two plates to form layers of about 1 cm, one of which was cooled with water (23 °C) and the other one stayed at room temperature without cooling. The product on the cooled plate had hardened after 24 minutes

(37 °C) and in the other pan after 36 minutes (49 °C). The products were kept overnight (23 °C), crushed once by a jaw crusher and analysed (Table 2).

Table 2a

The chemical analyses of the end products in Tests 1a and 1b

	Test 1a	Test 1b
N-kok %	17.0	16.5
NH ₄ -N %	10.3	10.6
Urea- N %	6.4	5.5
P ₂ O ₅ -KM %	39.3	40.0
P ₂ O ₅ -ASL	28.3	29.0
P ₂ O ₅ -VL	39.3	39.5
H ₂ O-KF %	5.8	7.6
pH	6.2	6.2

On the basis of an X-ray diffraction analysis, the end product contained mono ammonium phosphate, ammonium sulphate, and urea.

Table 2b

The physical properties of non-granulated end products

(* The sample was crushed before the analysis)

Property	Test 1a	Test 1a*	Test 1b	Test 1b*
Granular strength [N]				
Mean value	46	27	29	19
Max. 5	62	33	37	22
Min. 5	29	20	22	16
Abrasion [%]	1.5	1.4	2.1	1.1
Moisture absorption [%], 80% RH				
2 h	0.9	2.3	1.3	2.4
4 h	1.9	4.4	2.3	4.3
6 h	2.6	6.2	3.3	6.3

The tests proved that the product was hard enough to be treated and that it was not too pulverulent. The velocities of the moisture absorption were in the same order as those of typical nitrate-based NPK fertilizers.

Example 2

The test used urea phosphate mother liquid, the composition of which was.

	H ₂ O-KF	40	%
	Urea-N	10.7	%
5	NH ₄ -N	0.34	%
	P ₂ O ₅ -tot	24.1	%
	P ₂ O ₅ -ws	23.2	%
	pH (10% aqueous solution)	1.7	

75 g of CaCO₃ were added to 1000 g of mother liquid and it was heated at 100-114 °C for one hour. The final moisture was 13% and the pH in a 10% solution was 5.0. The suspension was dried for 3.5 hours at 60 °C.

The chemical analysis of the product:

	H ₂ O-KF	3.0	%
	Urea-N	10.3	%
15	NH ₄ -N	5.3	%
	P ₂ O ₅ -km	37.7	%
	P ₂ O ₅ -vl	25.4	% (67%)
	P ₂ O ₅ -asl	37.7	% (100%)
	pH (10%)	4.9	

Example 3

A continuous test was conducted by using a 5-litre reactor and by continuously feeding to the heated reactor the same mother liquid as in Example 2, and by simultaneously feeding calcium carbonate. The viscosity was adjusted by adding water. No ammonia could be observed in the exhaust gases. The conditions during the run were as follows:

	Reaction time	3.5 h
	Reactor temperature	105-110 °C
	Reactor pH	4.5-5.0
	Moisture of suspension	10-12%
30	Consumption of carbonate	135g/1000g ML
	Added water	185g/1000g ML
	Viscosity	300 cP

The suspension was dried at 60 °C and the chemical analysis of the dried product was:

	H ₂ O-KF	0.2-1.0	%	
	Urea-N	9.2	%	
5	NH ₄ -N	6.1	%	
	P ₂ O ₅ -km	36.4	%	
	P ₂ O ₅ -vl	28.7	%	(78%)
	P ₂ O ₅ -asl	36.4	%	(100%)
	pH (10%)	4.9		
10	N/P ₂ O ₅ ratio	0.420		

Example 4a

Urea phosphate mother liquid (1.865 kg) of the same quality as in Example 2 was fed into a 2.5-litre reactor that was provided with agitation and heating. Potassium carbonate (417 g) was continuously fed into the reactor and the suspension was agitated at 60 °C for 1.5 hours, so that the pH of the suspension (a 10% aqueous solution) increased from 2 to 4.1. The suspension was dried on a plate (93 °C) overnight. Table 3 shows the chemical analysis of the product.

Example 4b

Urea phosphate mother liquid (1.43 kg) of the same quality as in Example 2 was fed into a 2.5-litre reactor provided with agitation and heating. Potassium carbonate (237g) was fed into the reactor and the suspension was agitated at 60 °C for 40 minutes, so that the pH (a 10% aqueous solution) increased from 2 to 2.7. The suspension was dried in a pan (93 °C) overnight. Table 3 shows the analyses of the end product.

Table 3

The chemical analysis of the end product in tests 4a and 4b

	Test 4a	Test 4b
N-kok %	12.4	14.6
NH ₄ -N %	4.2	5.8
Urea- N %	8.2	8.8
P ₂ O ₅ -KM %	33.4	36.1
P ₂ O ₅ -ASL	33.4	36.1
P ₂ O ₅ -VL	26.2	28.2
K ₂ O-KM	18.6	14.2
H ₂ O-KF %	3.3	0.48
pH	6.6	6.5

Example 5

- 5 A product suspension (111 °C, pH 5.6, 1400 cP, moisture of 11.9%) that had been made on the continuous-action principle as in Example 1a by using a mother liquid of the same quality as in Test 2, but in a more diluted form (46% of H₂O, 8.9% of N, 20.4% of P₂O₅, pH 1.7) was allowed to cool to 35 °C and solidify on a plate as a 1.5 cm layer for 35 minutes.
- 10 2% of CaO was added to one part and it was ground and fed through an aperture plate. The other part was treated by a corresponding method but without adding CaO. In the starting position, the cooled product contained 10% of moisture. After three hours of drying (60 °C) the sample that included calcium oxide contained 4.7% of moisture and the reference sample, without the addition of CaO, contained
- 15 5.2% of moisture.

The untreated sample released all water (an end moisture of 0.3%), when drying was continued for 19 hours. The sample that had been treated with calcium oxide bound part of the water into a non-volatile form (an end moisture of 3.5%).

Example 6

- 20 As starting material, a mixture was used, which contained scrubber solution from the NPK fertilizer process, and phosphoric acid.

A solution having the composition of a scrubber solution from an NPK process was prepared by preparing a sludge from 2 kg of water and 2 kg of urea-based fertilizer containing 17.2% P_2O , 15.4% K_2 , 13.1% N (urea) and 1.7% N (ammonium). To this solution (sludge), fertilizer grade phosphoric acid was added (Siilinjärvi; 53.6% P_2O_5) and the thus obtained starting mixture was heated in a mixed reactor for the evaporation of water during 3 hours, at which point a temperature of 115 °C was reached. The moisture of the obtained sludge was 16% H_2O , its viscosity was 20 cP and its pH was 2.5.

To the reactor, 1.8 kg of the starting material mixture was added and the heating was continued for 3.8 hours to a final temperature of 115 °C, at which stage the moisture of the obtained sludge was 12% H_2O , the viscosity was 3,500 cP and the pH was 4.0. In order to prevent foaming, an anti-foaming agent (Fennodefo 380) had been added.

The sludge was poured on a plate for cooling, and it was immediately solidified. The cooled product was analysed without further drying and the analytical results are shown in Table 4.

Table 4

The chemical analysis of the end product of Example 6

N-tot %	6.9
NH_4 -N %	5.9
Urea-N %	1.0
P_2O_5 -KM %	40.8
P_2O_5 -ASL	36.3
P_2O_5 -VL %	32.2
K_2O -KM %	7.4
H_2O -KF %	8.7
pH	3.8

Claims

1. A method for manufacturing a solid ammonium phosphate and/or urea ammonium phosphate product from a solution containing urea and phosphoric acid, characterized in that

5 a) the solution containing urea and phosphoric acid is heated by mixing in order to evaporate water and to decompose the urea into carbon dioxide and ammonia;

b) the formed carbon dioxide is removed;

c) the formed ammonia is used to neutralize the phosphoric acid in the solution, and

10 d) the formed ammonium phosphate and/or urea ammonium phosphate suspension is further processed to form a solid ammonium phosphate and/or urea ammonium phosphate product.

2. A method according to Claim 1, characterized in that in the solution containing urea and phosphoric acid, the molar ration of the nitrogen of the urea and the phosphor of the phosphoric acid (N/P) is > 0.85 .

3. A method according to Claim 1 or 2, characterized in that the solution containing urea and phosphoric acid is the mother liquid of a urea phosphate process.

4. A method according to Claims 1 to 3, characterized in that solid matter, such as carbonate, sulphate, and oxide of alkali metals or alkaline earth metals and/or chloride, is added to the reaction mixture to partly neutralize the solution, to bind water and/or to add nutrients to the end product.

5. A method according to Claim 1, 2 or 4, characterized in that the solution containing urea and phosphoric acid is the scrubber solution of a urea-based NPK process, which contains or to which has been added phosphoric acid.

6. A method according to Claims 1 to 5, characterized in that the solution containing urea and phosphoric acid is heated at 50-125 °C.

7. A method according to Claim 6, characterized in that said solution is heated until the moisture of the formed suspension is 15-20%.

8. A method according to Claim 6 or 7, characterized in that said solution is heated until the pH of the suspension is 2.5-7.

9. A method according to Claim 6, 7 or 8, characterized in that the solution is heated until the molar ratio of the nitrogen of the ammonia and the phosphor of the phosphate (N/P) in the suspension is about 0.1-1.5 : 1.

10. A method according to Claims 1 to 9, characterized in preferably being continuous and diphasic: in the first phase, water is evaporated in one or more reactors at about 100 °C, until the moisture of the formed suspension is < 20% and the pH is 3-5 and, in a second phase, evaporation is continued in one or more reactors at about 110-115 °C, until the moisture of the suspension is < 10% and its pH is about 6-6.5.

11. A method according to Claims 1 to 10, characterized in that the product suspension containing ammonium phosphate and/or urea ammonium phosphate is solidified in the form of a layer of 1-30 mm, preferably 10mm in thickness, spread on a sheet-iron belt conveyor, which can be heated and/or cooled, and which is heated and/or cooled for 0.01-2 hours, preferably at a retention time of 0.05-0.5 hours to a final temperature of < 50 °C.

12. A method according to Claims 1 to 11, characterized in that the solidified end product is dried, crushed, ground and/or granulated.

13. A solid ammonium phosphate and/or urea ammonium phosphate product, characterized in being manufactured by the method according to any of the preceding Claims.

14. The use of the urea phosphate product according to Claim 13 as a fertilizer either as such or as a component of a mixed fertilizer.

15. A method according to Claim 3, characterized in that the solution containing urea and phosphoric acid is heated at 100-115 °C.

16. A method according to Claim 3 or 15, characterized in that the solution containing urea and phosphoric acid is heated until the moisture of the formed suspension is < 10%.

17. A method according to Claim 3, 15 or 16, characterized in that the solution is heated until the pH of the suspension is 4-6.5.

18. A method according to any of Claims 3, 15-17, characterized in that said solution containing urea and phosphoric acid is heated until the molar ratio of the ammonia nitrogen and the phosphate phosphor (N/P) in the suspension is about 0.85-1.5:1, preferably 1.3-1.4:1.

5 19. A method for the simultaneous manufacture of urea phosphate and a solid ammonium phosphate and/or urea ammonium phosphate product, in which the urea phosphate is manufactured by any known method, characterized in that the solid ammonium phosphate and/or urea ammonium phosphate product is manufactured from a solution containing urea and phosphoric acid so that:

10 a) the solution containing urea and phosphoric acid is heated by mixing in order to evaporate water and to decompose the urea into carbon dioxide and ammonia, and

b) the formed carbon dioxide is removed, and

15 c) the formed ammonia is used to neutralize the phosphoric acid in the solution, and

d) the formed ammonium phosphate and/or urea ammonium phosphate suspension is further processed to form a solid ammonium phosphate and/or urea ammonium phosphate product.

United States Patent [19]

Lewis et al.

[11] Patent Number: 4,461,913

[45] Date of Patent: Jul. 24, 1984

[54] PRODUCTION OF UREA PHOSPHATE

[75] Inventors: Harry T. Lewis; Ewell F. Dillard,
both of Florence, Ala.

[73] Assignee: Tennessee Valley Authority, Muscle
Shoals, Ala.

[21] Appl. No.: 376,809

[22] Filed: May 10, 1982

Related U.S. Application Data

[63] Continuation of Ser. No. 324,515, Nov. 24, 1981, now
Defensive Publication No. T. 103,206.

[51] Int. Cl.³ C07C 126/08; C07C 127/01;
C07F 15/04

[52] U.S. Cl. 564/063; 260/439 R;
564/73

[58] Field of Search 564/63, 73; 260/439 R

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Primary Examiner—Robert V. Hines

Attorney, Agent, or Firm—Robert A. Petrussek

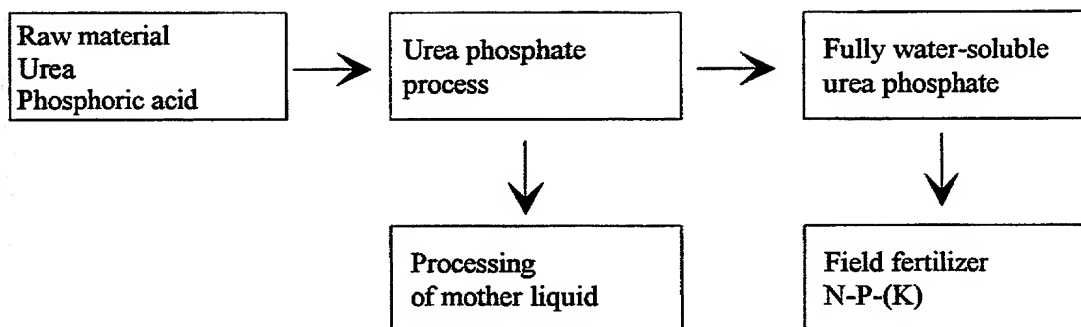
[57] ABSTRACT

A two-stage continuous crystallization process for production of urea phosphate by reaction of impure wet-process orthophosphoric acid (about 54 percent P_2O_5) and urea with simultaneous addition of a selected acidifying agent (sulfuric acid, hydrochloric acid, or phosphoric acid) to clarified mother liquor used as recycle in the process. Addition of the acidifying agent decreases pH in the crystallization process whereby the solubility of a contaminating water-insoluble iron phosphate-urea salt $[FeH_3(PO_4)_2 \cdot 2CO(NH_2)_2]$ is increased, purity of the crystalline urea phosphate product is improved significantly, and the useful storage life of the recycle mother liquor is prolonged.

8 Claims, 4 Drawing Figures

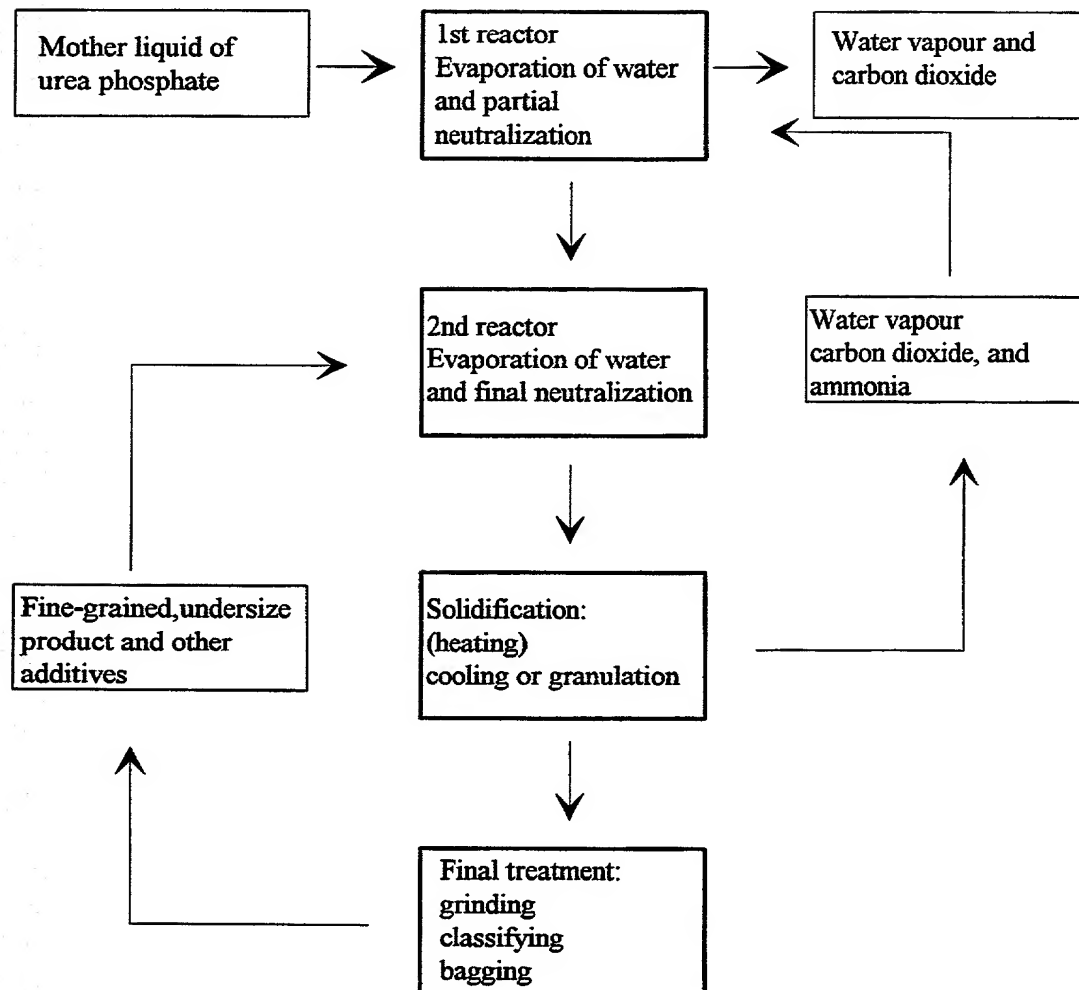
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Flow chart 1



2 / 2

Flow chart 2



BIRCH, STEWART, KOLASCH & BIRCH, LLP

P.O. Box 747 • Falls Church, Virginia 22040-0747
Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

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Method for treating fertilizer process solutions

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Prior Foreign Application(s)			Priority Claimed	
<u>991563</u>	<u>Finland</u>	<u>July 8, 1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Month/Day/Year Filed)	Yes	No
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(Number)	(Country)	(Month/Day/Year Filed)	Yes	No
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BIRCH, STEWART, KOLASCH & BIRCH, LLP or **CUSTOMER NO. 2292**

P.O. Box 747 • Falls Church, Virginia 22040-0747

Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

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Inventor, if any:
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GIVEN NAME/FAMILY NAME <u>Janne KARONEN</u>		INVENTOR'S SIGNATURE <u>Janne Karonen</u>	DATE* 8 March 2002
Residence (City, State & Country) <u>Helsinki, Finland</u> <u>FIX</u>		CITIZENSHIP Finnish	
MAILING ADDRESS (Complete Street Address including City, State & Country) <u>Puustellinpolku 12 D 25, FIN-00410 Helsinki, Finland</u>			
GIVEN NAME/FAMILY NAME <u>Anders WECKMAN</u>		INVENTOR'S SIGNATURE <u>Anders Weckman</u>	DATE* 8 March 2002
Residence (City, State & Country) <u>Espoo, Finland</u> <u>FIX</u>		CITIZENSHIP Finnish	
MAILING ADDRESS (Complete Street Address including City, State & Country) <u>Mikkelaentie 15 D 8, FIN-02770 Espoo, Finland</u>			
GIVEN NAME/FAMILY NAME		INVENTOR'S SIGNATURE	DATE*
Residence (City, State & Country)		CITIZENSHIP	
MAILING ADDRESS (Complete Street Address including City, State & Country)			
GIVEN NAME/FAMILY NAME		INVENTOR'S SIGNATURE	DATE*
Residence (City, State & Country)		CITIZENSHIP	
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